

Characterization and Reconstruction of Historical London, England, Acidic Aerosol Concentrations

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Several past studies of the historical London air pollution record have reported an association between daily mortality and British Smoke levels. However, this pollution index does not give direct information on particulate mass or its chemical composition. A more specific particulate matter index, aerosol acidity, was measured at a site in central London, and daily data are available for the period 1963-1972. British Smoke and SO₂ were also measured at the same site. Also, meteorological parameters were routinely measured at a nearby British Meteorological Office. Thus, daily fluctuation of the acidic aerosols was characterized in terms of other environmental parameters. Each of the other parameters analyzed seems necessary, but not sufficient to explain a high level of acidic aerosol. Overall, about half of the variance of log-transformed daily fluctuations of acidic aerosols can be explained by a combination of parameters including SO₂ and British Smoke concentrations, temperature, ventilation by wind, and humidity. The rest of the variance cannot be explained by the parameters included in this analysis. Potential factors responsible for this unique variance would be variations in the availability of basic gases to cause neutralization and variation in the availability of catalytic metal salts. Because the acidic aerosol has a unique component of variation, it may be possible to distinguish health effects due to this specific pollutant from other available pollution indices or environmental factors.

Introduction

A relationship between air pollution and mortality/morbidity was recognized in England, especially after the severe London fog episode of December 5-8, 1952 (e.g., maximum sulfur dioxide and British Smoke levels were 1.34 ppm and 4.46 mg/m³ 24-hr average, respectively). Although sulfuric acid was considered as one of the possible pollutants that could be responsible for the increased mortality and morbidity (1), routine air pollution monitoring conducted by local authorities and other regulatory bodies did not include direct observations for acidic aerosol. Shortly after the 1952 episode, the Air Pollution Research Unit at St. Bartholomew's Hospital started a major research program on air pollution (2). Their daily measurements of British Smoke (BS) and sulfur dioxide (SO₂) began at the hospital in January 1954 (Fig. 1). Also, concentrations of other pollutants, including sulfuric acid (H₂SO₄), were initially measured intermittently (during episodes), and later, on a daily basis. In this paper, the resulting historical London acidic aerosol

record is characterized, especially in comparison to other measured pollutants. The possibility of a predictive formula for London acidic aerosol is considered.

Characterization of the Historical London Acidic Aerosol

Before attempts can be made to assess the historical health impact of London acidic aerosol exposures, it is important to review how the measurements were made and how the London acidic aerosol has been characterized in past literature. We describe the exposures and compare them with those for other environmental parameters that may be related to the variation of levels of the acidic aerosol exposures.

Brief Literature Review

According to the summary of a 10-year study (1954-1964) by the Air Pollution Research Unit at the St. Bartholomew's Hospital (2), the highest daily and hourly acid concentrations (expressed as sulfuric acid) recorded were 347 µg/m³ and 678 µg/m³, respectively, on an episodic day in December 1962. The measure-

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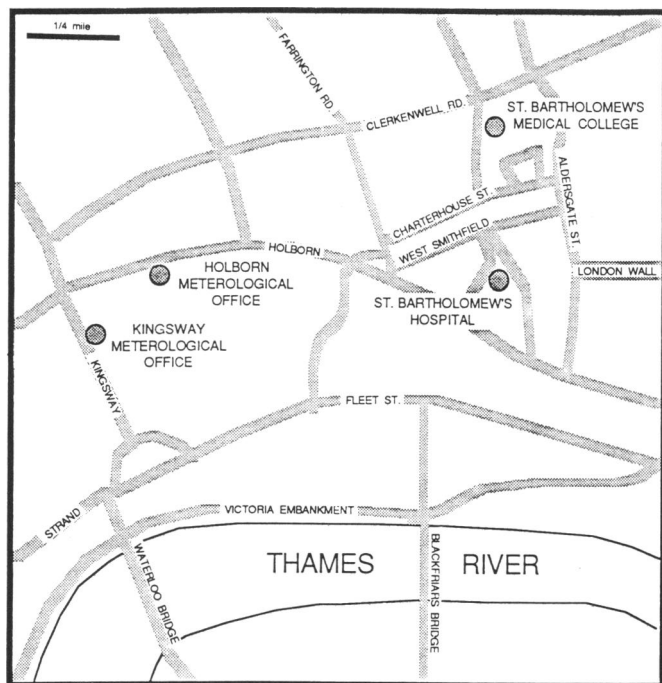


FIGURE 1. Location of London, England, central city sites for pollution and meteorological parameters.

ment of H_2SO_4 during pollution episodes began in 1957. The daily measurements of aerosol acidity at the Medical College of St. Bartholomew's Hospital were initiated in April 1963. The daily levels from that time through 1972 are shown in Figure 2, and annual and winter season (November 1 through February 29) averages, standard deviations, and maximums are noted. It can be seen that aerosol acidity levels were usually highest during the winter, apparently due to increased heating fuel usage combined with adverse meteorological conditions.

The analytical method of the aerosol acidity determination was reported in detail by Commins (3). The particulate matter in the air was collected by filtration at 10 to 20 L/min, and the filter was subsequently immersed in a known excess of 0.01 N sodium tetraborate and titrated back to pH 7 with 0.01 N sulfuric acid. The procedure allows the sodium tetraborate to neutralize the acid before the potentially interfering insoluble bases do. The potential interferences by acidic gases, basic gases, and other particulate acids were reported to be negligible. Based on the fact that there was no correlation between chloride and acidity and that sulfates were highly correlated with acidity, Commins suggested that the predominant acid present in the air was H_2SO_4 . However, Commins also mentioned that sulfate was always present in amounts greater than could be accounted for by H_2SO_4 alone, apparently indicating the presence of partially or totally neutralized sulfate species as well. Junge and Scheich, who determined the hydrogen ion concentrations in aerosols in Mainz, Germany, by dissolving the aerosol specimen in water and determining

the pH values of these very dilute solutions, noticed that a comparison of results indicated a considerably higher acid concentration in London. They conducted an experiment in the winter of 1967–1968 using the two different analytical methods on samples from both the German sites and the London site in order to determine causes for the difference (4). Their results, comparing the SO_4^{2-} and H^+ values for London confirmed that the H^+ (as sulfuric acid) concentration was essentially due to H_2SO_4 . Thus, although these data represent titratable acid concentrations, most was apparently present as the strong acid H_2SO_4 .

Microscopic examination of the London acid aerosol was made in 1959 by Waller (5). Cascade impactor samples were collected onto slides impregnated with indicators. Waller observed that most of the large acid droplets on the first and second stages (effective mean drop sizes of 23 and 13 μm , respectively) contained solid particles. It was also noted that a substantial fraction of the acid aerosol was collected on the backup filter (effective mean drop size 0.5 μm), especially when the relative humidity was lower than 85%, and that much of the smoke was also collected on the filter. Junge and Scheich also compared the ion concentration in different size ranges. Using a single-stage impactor and a parallel filter, they determined H^+ concentrations in two size ranges: Aitken nuclei ($r < 0.1 \mu\text{m}$) and large and giant ($r > 0.1 \mu\text{m}$) particles. For the London samples, they measured about nine times more titrated acidity in the Aitken range than in large and giant range.

Relationships Between Daily Acidic Aerosol Concentration and Other Pollution Indices and Weather Parameters

As daily measurement of BS and SO_2 were also made at the Medical College of St. Bartholomew's Hospital, the daily fluctuations of these pollution indices can be compared with those of total aerosol acidity from 1963 onward, when daily total aerosol acidity records became available. Furthermore, meteorological records such as temperature, humidity, and visual range were measured at the London Meteorological Office, located close to the Medical College (Fig. 1). Thus, daily fluctuation of those parameters can be compared with the total aerosol acidity. For this study, a data set for the winter periods (November 1–February 29) between 1963 and 1971 was examined because winter periods tend to have the highest pollution levels and have therefore been the subject of past observational mortality studies. Descriptive statistics for the data set are shown in Table 1.

It was reported that at the sampling location in central London the smoke measured came mainly from domestic sources some distance away, and much of the SO_2 was from central heating installations in commercial buildings (2). H_2SO_4 , or its precursor, sulfur

trioxide (SO_3), could be emitted from both sources. Also, fluctuations in the levels of these three pollution indices must have been influenced by adverse meteorological conditions, e.g., temperature inversions,

which inhibit the dispersion of pollutants.

In Table 2, correlation coefficients among key pollution and meteorological parameters for the 1963–1971 winter periods are shown. However, because the

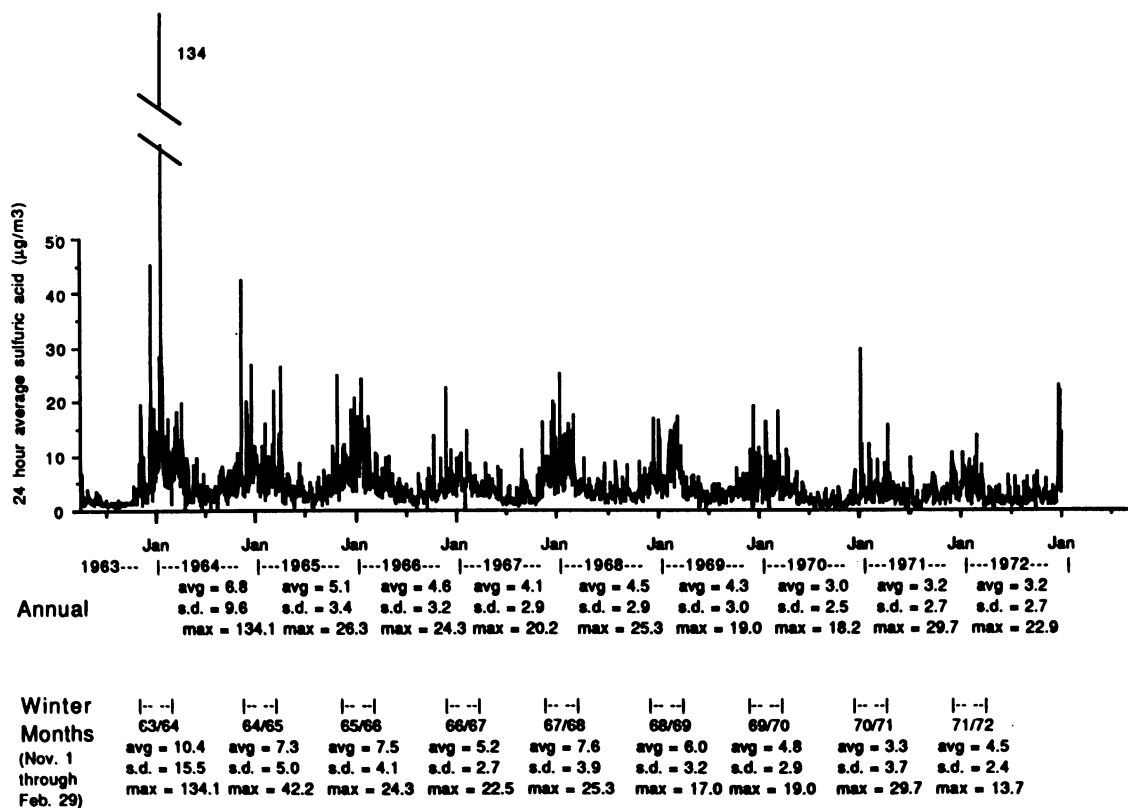


FIGURE 2. Historical London daily aerosol acidity data (total H^+ as H_2SO_4).

Table 1. Descriptive statistics of pollution indices and meteorological parameters in London 1963–1971 winters.^a

Statistics	Acidity, $\mu\text{g}/\text{m}^3$ ^b	BS, $\mu\text{g}/\text{m}^3$ ^c	BS, $\mu\text{g}/\text{m}^3$ ^b	SO_2 , $\mu\text{g}/\text{m}^3$ ^c	SO_2 , $\mu\text{g}/\text{m}^3$ ^b	Temperature, Celsius	Humidity, % ^b	Wind speed, knot ^d
Mean	6.5	102	92	241	317	5.6	80.0	9.5
Median	5.3	77	72	210	282	5.7	81.0	9.0
SD	6.7	85	71	126	163	3.6	10.1	4.0
Maximum	134.1	734	709	1231	1298	16.3	100	23.2

^aWinters, November 1–February 29; $n = 962$.

^bMeasurements at the Medical College of St. Bartholomew's Hospital in central London.

^cMean of seven sites for greater London.

^dMeasurement at Heathrow Airport.

Table 2. Correlation matrix of pollution indices and meteorological parameters in London 1963–1971 winters.^a

Index	Acidity ^b	BS ^c	BS ^b	SO_2 ^c	SO_2 ^b	Temperature ^b	Humidity ^b
BS ^c	0.485						
BS ^b	0.655	0.753					
SO_2 ^c	0.544	0.887	0.738				
SO_2 ^b	0.569	0.611	0.723	0.675			
Temperature ^b	-0.298	-0.233	-0.314	-0.391	-0.315		
Humidity ^b	0.179	0.228	0.206	0.166	0.133	0.110	
Inv. Wind ^d	0.393	0.515	0.653	0.527	0.509	-0.186	0.159

^aWinters, November 1–February 29. $n = 962$.

^bMeasurements at the Medical College of St. Bartholomew's Hospital in central London.

^cMean of seven sites for greater London.

^dMeasurement at Heathrow Airport.

data were collected in a time series and may also be of non-normal distributions, interpretation of simple correlation coefficients can sometimes be misleading. Thus, those relationships are also examined using bivariate scatter, cross-correlation, and autocorrelation plots.

In Figure 3, scatter plots of aerosol acidity versus other pollution indices and meteorological variables for 1963–1970 winters are shown (1971–1972 acid data were available, but excluded from this analysis for consistency because wind data were missing for this period). Aerosol acidity has a fairly linear relationship with BS for the lower range, but the variability increases as the levels go up. The same phenomenon can be observed in the SO_2 and aerosol acidity plot except that the highest SO_2 does not coincide with the highest aerosol acidity, and elevated acid concentrations occur even in the lower range of SO_2 . If a majority of the H_2SO_4 was directly emitted as H_2SO_4 along with SO_2 , then levels of H_2SO_4 might be expected to show linearity with SO_2 . If the observed higher values, which seem to exhibit a straight line, are the limit of SO_2 to acid relationship, then some other factor(s) must have suppressed the measured levels of acidity on other days with sufficient SO_2 or SO_3 for conversion. One possible

mechanism for this phenomenon would be neutralization of the H_2SO_4 formed in the atmosphere. Another possibility would be variation in the availability of potentially catalytic salts such as those of manganese and iron. Unfortunately, daily measurements of total sulfates to match these acid data, which would have been an indicator of the extent of neutralization, are not available. However, it may be possible to estimate amount of sulfates from existing visual range records, since it has been shown that visual range-derived extinction coefficient often has a fairly linear relationship with fine mass (6). Although carbonaceous mass may also largely influence the extinction, its contribution can be subtracted out from the total extinction (7) on the basis that BS is a good estimator of total carbon concentration in London (8).

Yet another important factor for catalytic oxidation of SO_2 to H_2SO_4 is humidity; however, as can be seen in Figure 3c, the relationship is again not a straight linear plot. What can be said from this figure is that it appears that elevated relative humidity was a necessary, but not a sufficient, factor for high acid levels in the historical London data.

Temperature and acid levels in this data set likely had an indirect relationship rather than a physical

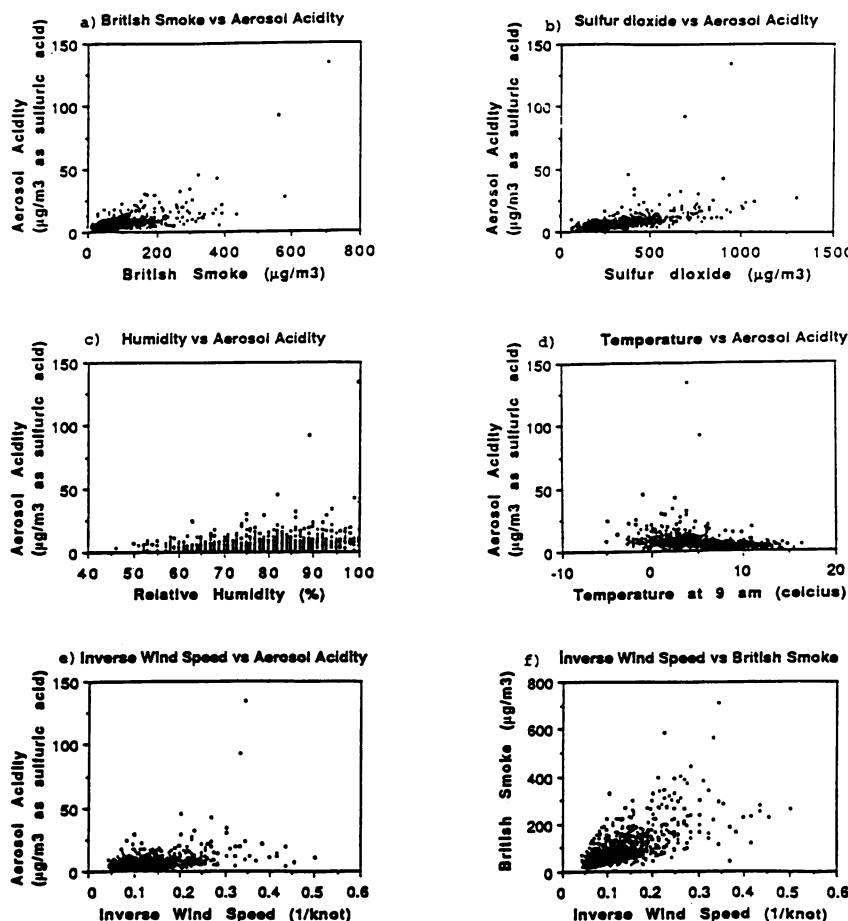


FIGURE 3. Scatter plots showing bivariate relationships between aerosol acidity and other environmental parameters.

one: Lower temperature leads to increased usage of heating fuel, resulting in higher pollutant emissions. Also, cold, clear nights lead to temperature inversions and associated poor dispersion of pollutants. This can be observed in the correlation matrix, where correlations between temperature and the three pollution indices vary to approximately the same extent. As shown in Figure 3*d*, the highest acid levels occurred in the middle range of temperature.

Winds also serve as an indicator of atmospheric dispersion. With the inverse of wind speed, the larger value of this index indicates less ventilation and the potential for elevated pollution levels. In Figure 3*f*, the relationship between BS and the inverse of wind speed is also shown next to that for aerosol acidity for comparison. BS has a more directly linear relationship with inverse of wind speed than aerosol acidity does, though variations get still larger at higher levels. Even the exclusion of the two highest points in the acid-inverse wind relation still failed to noticeably improve overall linear relation (the correlation coefficient only rises from 0.39–0.43).

All the data considered in this analysis are 24-hr averages except temperature and humidity, which are the 9:00 A.M. observations at the Meteorological Office in central London. It was reported that maximum concentrations usually occurred between 8:00 and 9:00 A.M. for SO₂ and 1 hr later for BS. A comparison of limited hourly records of BS and SO₂ measured between 9:00 and 10:00 A.M. with those of 24-hr averages reflects this. Conversely, the recorded hourly acid levels measured between 9:00 and 10:00 A.M. are usually lower than the 24-hr average of the same day, probably indicating occurrences of the highest acid levels at a different hour than those of the two other pollution indices. Since hourly measurements of the three pollution indices throughout a day are not available, it is difficult to investigate the behavior and interactions of the three in a smaller time increment than a day. However, day-to-day fluctuation of the pollution and meteorological parameters can be examined comprehensively from this data set.

In Figure 4, cross-correlations of a composite winter data set (1963–1971) are shown for up to 15 days of lag. For this calculation, 15 days of missing values were inserted between each of the eight winters in order to avoid inappropriate cross-correlations between winters. By combining the eight winters, any fortuitous variation in a certain individual year would be attenuated, and variations common to most of the winters would be extracted. One advantage of cross-correlation is that it can detect causal relationship between two parameters if one parameter is affecting the other parameter with a delayed time increment: if the plot of correlation over plus and minus lags becomes non-symmetric, then causality between the variables may be implied. Of course, if the time lag of effect is smaller than time increment in which the parameters are measured, then such effects will not be observed. If a certain factor is influencing two parameters simulta-

neously, then cross-correlation between the two parameters will be symmetric. This seems to be the case with the relationship between aerosol acidity and the other two pollution indices shown in Figure 4, with the highest correlation occurring on the same day. The correlation coefficient between central London BS and aerosol acidity (0.66) is slightly higher than the correlation between aerosol acidity and central London SO₂ (0.57), and the correlation between the central site BS and the central site SO₂ was even higher (0.72). The cross-correlation between aerosol acidity and temperature suggests causality possibly due to increased emissions following low temperatures. Humidity and aerosol acidity have a slightly positive relationship, but as could be seen in the scatter plot, the relationship is not stable linearly. Cross-correlation between the inverse of wind speed and aerosol acidity is skewed toward the upper right quarter: Apparently, today's calm wind can cause tomorrow morning's stagnated pollution levels.

Autocorrelations of pollution and meteorological parameters for the composite winter data (1963–1971) are shown in Figure 5. The long tail seen in the cross-correlation figures can be understood if we notice that each variable has its own autocorrelation, either because the variable itself has such a nature, as in the case with the temperature, or because the variable is influenced by some other variable that has autocorrelation over time, or a combination of both. Again, it should be noted that any random shock in an individual year would be averaged out and that consistent trends for the overall data are extracted in this calculation. Thus, autocorrelations for each individual year tend to have less long-lasting autocorrelation characteristics, due to larger influence of random disturbances on smaller sample sizes. It can be seen that the temperature has the highest autocorrelation, and the humidity has the smallest autocorrelation. Autocorrelation of inverse wind speed is of relatively "short memory." A characteristic seen in autocorrelations of BS and SO₂ are the peaks around 7- and 14-day lags, probably reflecting the weekly emission pattern. This pattern was not as clear in most of the individual year's autocorrelations. This emission pattern is not seen in the autocorrelation of aerosol acidity, however, indicating that variations caused by other factors were more significant, perhaps a contribution from secondary acid aerosol formation.

Reconstruction of Daily Aerosol Activity

In the previous section, daily fluctuations of aerosol acidity were characterized in terms of bivariate relationships with other pollution and meteorological parameters. In this section, an attempt is made to describe the daily fluctuations of aerosol acidity in terms of a multivariate relationship with the other parameters using multiple regression. It should be noted that,

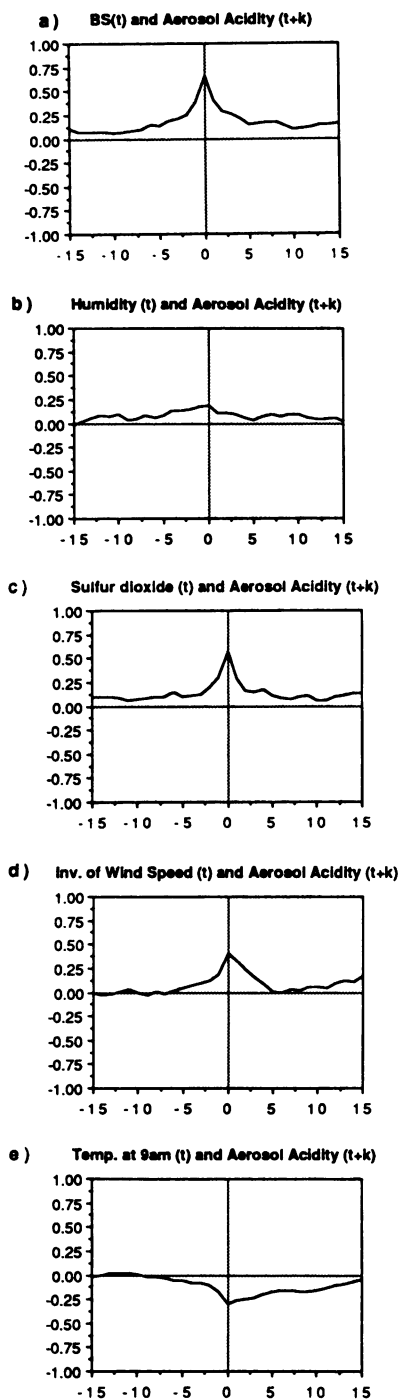


FIGURE 4. Cross-correlation of composite winter data, 1963 to 1971; pollution indices and meteorological parameters (t) versus aerosol acidity ($t+k$). Y-axis: cross correlation coefficients; X-axis: lag in day k .

since a number of correlated factors are influencing the variation of aerosol acidity levels, the coefficients of regression equations employing these variables cannot necessarily be interpreted in a physically meaningful manner.

Because what is sought is a comprehensive predictive model, no outlier was eliminated from the data set.

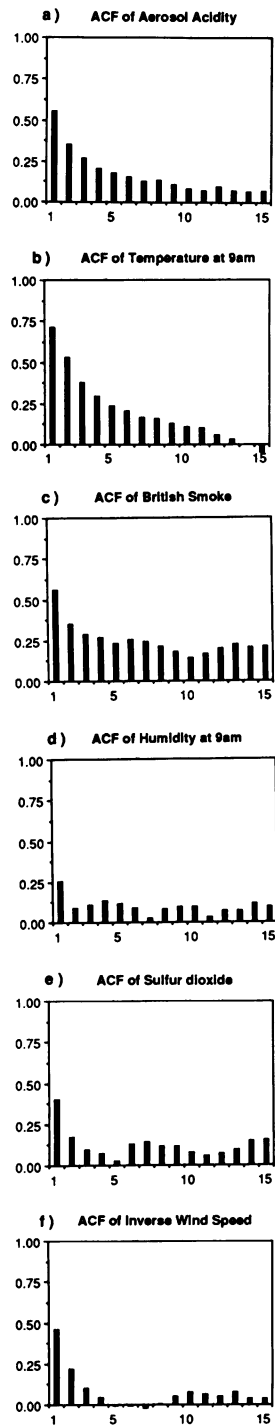


FIGURE 5. Autocorrelation (ACF) of pollution and meteorological parameters for composite winter data, 1963 to 1971. X-axis: lag in days.

Rather, the effect of the outliers was examined. As described in the previous section, most bivariate scatter plots showed higher variance for higher values, and initial trials of stepwise regression resulted in a model that violated two of the assumptions in linear regression: The residuals were not normally distributed and residuals were larger for the larger values, indicating

model heteroscedasticity. Thus, a transformation was required (9). Square root transformation of the aerosol acidity improved the residual diagnostics, but still showed similar trends. Therefore, an even stronger function, a natural logarithmic transformation, was employed, and the two residual problems were resolved. The resulting regression equation for the entire data set ($n = 953$) is:

$$\begin{aligned} \ln(AA) = & 0.208 + 9.34 \times 10^{-4} BS \text{ (10.25)} \\ & + 2.04 \times 10^{-3} SO_2 \text{ (263.92)} - 5.41 \times 10^{-2} T \text{ (171.08)} \\ & + 1.26 \times 10^{-2} H \text{ (78.39)} \end{aligned} \quad [1]$$

$$R^2 = 0.58 \text{ (adjusted for degrees of freedom)}$$

where AA = 24-hr average aerosol acidity expressed as $\mu\text{g}/\text{m}^3$ of H_2SO_4 ; BS = 24-hr average British Smoke in $\mu\text{g}/\text{m}^3$, as determined by locally developed empirical calibration; SO_2 = 24-hr average SO_2 in $\mu\text{g}/\text{m}^3$; T = temperature at 9:00 A.M. Celsius; H = relative humidity at 9:00 A.M. percent; and the numbers in parentheses are corresponding F -ratio of the coefficients.

Furthermore, based upon visual inspection of the bivariate relationships, the data were separated into two data subsets: BS less than $200 \mu\text{g}/\text{m}^3$ and BS greater than $200 \mu\text{g}/\text{m}^3$, and regressions were performed to see if any systematic difference actually exists between higher and lower values. The resulting regression for days with BS greater than $200 \mu\text{g}/\text{m}^3$ ($n = 64$) was:

$$\begin{aligned} \ln(AA) = & -0.561 + 3.19 \times 10^{-3} BS \text{ (20.46)} \\ & + 1.01 \times 10^{-3} SO_2 \text{ (11.66)} - 6.92 \times 10^{-2} T \text{ (9.94)} \\ & + 2.11 \times 10^{-2} H \text{ (8.35)} \end{aligned} \quad [2]$$

$$R^2 = 0.51 \text{ (adjusted for degrees of freedom)}$$

The regression for days with BS less than $200 \mu\text{g}/\text{m}^3$ ($n = 889$) was:

$$\begin{aligned} \ln(AA) = & 0.188 + 2.45 \times 10^{-3} SO_2 \text{ (489.47)} \\ & - 5.39 \times 10^{-2} T \text{ (171.39)} + 1.23 \times 10^{-2} H \text{ (75.27)} \end{aligned} \quad [3]$$

$$R^2 = 0.53 \text{ (adjusted for degrees of freedom)}$$

Thus, inverse of wind speed was not retained in any of the subset regressions above, but, as can be seen in Figure 3f, this may be due to the colinearity between BS and inverse of wind speed. Apparently, BS explains much of the variance due to the ventilation factor, along with pollution emission variance. For BS less than $200 \mu\text{g}/\text{m}^3$, BS was not included as a significant variable, probably because BS , as the data set divider criterion, has now reduced its explanatory power. The separate models do not give better fits than the overall model. Many of the F -ratios of the regression appear to be large, but interpretation requires caution because this logarithm-transformed data still has one remaining residual diagnostic problem: The Durbin-Watson statistics for the overall model was 1.00, which

indicates that the null hypothesis of positive autocorrelation in the residual cannot be rejected. Thus, the error variance of this regression by the least squares method could be underestimated and the significance of the coefficient overstated. The cause for this autocorrelation in the residual may be either due to the autocorrelation in the predictor variables or due to the autocorrelation of a portion of the variance that could not be explained by the linear combination of the predictor variables. More confident estimates of regression coefficients may be obtained either by employing weighted least squares (10) or by applying autoregressive modeling methods.

Summary and Conclusion

In historical London air pollution, over half of the variance of daily fluctuations of acidic aerosols can be explained by a combination of factors including SO_2 and BS concentrations, temperature (which also influences pollution emission and dispersion rates), ventilation by wind, and humidity (which may enhance the catalytic oxidation of SO_2). Each one of the factors seems necessary, but not sufficient to explain a high level of acidic aerosol. The rest of the variance cannot be explained by the parameters included in this analysis. Thus, the acidic aerosol had a fairly large portion of unique daily fluctuation, especially on the elevated pollution days. Potential causes for this uniqueness include variations in the availability of gases such as ammonia to cause the neutralization of acids to less acidic sulfates, or variations in the availability of such catalytic metal salts as those of manganese and iron (which may enhance catalytic conversion of SO_2 to H_2SO_4). In either case, identification of this variation would require measurements of either sulfates and/or metal concentrations, neither of which was routinely measured. However, there is a possibility of estimating the concentration of airborne sulfate from routinely measured visual range records, and it may also be that the presence of neutralizing and/or catalytic substances are associated with specific wind directions or synoptic weather conditions. Thus, there are several avenues of future research open that may allow further improvements in the power of such predictive formulae. The utility of a multiple regression incorporating an index of visual range is currently under investigation.

The results of this research also have an interesting implication in terms of health effect assessment of acidic aerosols. Since acidic aerosol also has a unique component of variation, it may be possible to distinguish the health effects due to this specific pollutant from other available pollution indices or environmental factors. In other words, if the daily fluctuation of acidic aerosol were completely explained by daily fluctuations of other available pollution and meteorological parameters, the effect of acidic aerosol would never be identified as a unique entity once the model

was controlled for the rest of the variables. This implies that it may well be possible to distinguish an acid aerosol health effect in this data set from those already reported for British Smoke and SO_2 .

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